

Block spin magnetism and metal-insulator transition in a two-dimensional Hubbard model with perfect vacancy superstructure

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We study the phase diagram of a square lattice Hubbard model with a perfect vacancy superstructure. The model can be also defined on a new bipartite lattice with each building blocks consisting of a minimal square. The non-interacting model is exactly solved and a mid-band gap opens at the Fermi energy in the weak inter-block hopping regime. Increasing the Coulomb interaction will develop the Néel antiferromagnetic order with varying block spin moments. The metal-insulator transition with U_{MI} smaller than the one without vacancies occurs above the magnetic instability U_M . The emergent intermediate magnetic metal phase develops substantially in the moderate inter-block hopping regime. Drastic increases in the ordered moment and the gap magnitude are observed on the verge of tight-binding band insulator with increasing U . The implications of these results for the recent discovered $(A,Tl)_yFe_{2-x}Se_2$ compounds are discussed.

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The discovery of superconducting iron pnictide materials have attracted enormous enthusiasm in searching for copper-free high temperature superconductors[1]. Recently, a family of ternary iron chalcogenides $(A,Tl)_yFe_{2-x}Se_2$ [2, 3] (with A being the alkali atoms) has been shown to exhibit superconductivity (SC) in proximity to a magnetic insulating phase. In the iron deficient compounds ($x > 0$) there are Fe-vacancies in the square lattice of the Fe-atoms. Interestingly, the Fe-vacancies could be ordered in certain periodic superstructures in $(K,Tl)Fe_{2-x}Se_2$ where the SC appears for $x = 0.12 \sim 0.3$ [3, 4]. The vacancy superstructures were reported in early Mössbauer experiment on the non-superconducting material $TlFe_{2-x}Se_2$ some years ago[5], and recent transmission electron microscopy experiment [6] provides clear evidence for the Fe-vacancy superstructures in the $KFe_{2-x}Se_2$ samples.

First principle calculations for $(K,Tl)Fe_{1.5}Se_2$ show that the Fe-vacancy orthorhombic superstructure can be stabilized in the ground states and play a crucial role in the electronic structures[7, 8]. The observed activation gap, which is about ~ 60 meV for $x \sim 0.5$, raises a concern as whether the insulating behavior is due to the antiferromagnetic (AFM) ordering itself, or due to the Fe-3d electron correlations. The band structure calculations in [8] provide evidence that a moderate Coulomb interaction is required in order to account for the sizable gap and a Mott localization can be enhanced due to the ordered vacancies. The paramagnetic (PM) Mott transition for $x = 0.5$ as well as possible s-wave SC in a doped Mott-insulator have been also proposed in a two-orbital model using spin-rotor mean-field (MF) theory[9, 10].

Here, we focus on another type of Fe-vacancy pattern, i.e., a tetragonal vacancy superstructure shown in Fig. 1(a). The advantages of this pattern is of two-folds. First, it is a perfect vacancy superstructure in the sense that it exhibits the maximal symmetry without breaking the in-plane four-fold rotational invariance and that all sites are equally three-coordinated (with vacancy density 20%)[11]. Second, this structure has been clearly observed in a number of

$(K,Tl)_yFe_{2-x}Se_2$ samples (for $x \sim 0.4$)[6, 12, 13]. Recent first principle calculations[11] show that the ground state of $(K,Tl)_yFe_{1.6}Se_2$ is a large block spin checkerboard or Néel AFM which is quite different to all previously known magnetic patterns in the iron-based materials. This novel AFM ordering pattern has been observed in recent neutron diffraction experiments[13–15]. It is due to this large spin magnetism that the parent material $(K,Tl)_{0.8}Fe_{1.6}Se_2$ could be an AFM insulator[11, 16].

These developments motivate us to study a simplified single orbital Hubbard lattice with the perfect vacancy superstructure. This model not only describes the Mott physics in the presence of the ordered vacancies, but also captures the geometry frustration as well as the structure distortion. Therefore, it can serve as a basic model system for the metal-insulator(MI) transitions and the complicated magnetic properties in the presence of the vacancy orderings. In this paper, we show that the interplay among the electron correlation, the geometry frustration, and the structure distortion in such a vacancy superstructure will result in a rich phase diagram.

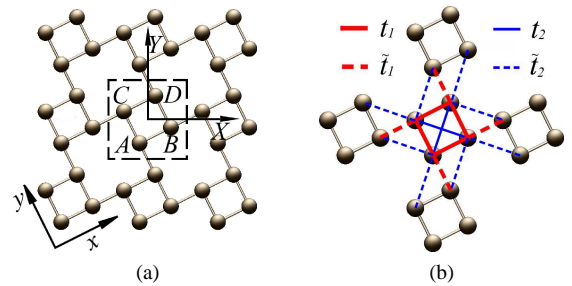


FIG. 1: (color online). (a) Square lattice with perfect vacancy superstructure: The dashed lines connect four neighboring vacancies enclosing a minimal square. All sites are equivalent with three coordinates. The x, y axes are for conventional Fe-Fe square lattice, while the X, Y axes are for the bipartite lattice of blocks. (b) The n.n. (red) and n.n.n. (blue) intra-block (solid) and inter-block (dashed) hopping amplitudes.

The Hamiltonian we studied is the Hubbard model

$$H = - \sum_{ij\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_i U n_{i\uparrow} n_{i\downarrow} + \sum_i \mu (n_{i\uparrow} + n_{i\downarrow}), \quad (1)$$

where $c_{i\sigma}$ is the annihilation operator for a Fe-3d electron at site i with spin $\sigma = \uparrow, \downarrow$; $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$ the electron number operator; t_{ij} the hopping parameters; U the on-site Coulomb interaction; and μ the chemical potential. As a peculiar feature of the vacancy superstructure, the whole lattice can be perfectly covered by fundamental square blocks enclosed by four neighboring vacancies under the periodic boundary condition, see in Fig.1(a), where the X, Y are the new axes for the block lattice. Then the four sites in each block can be labeled by $A = (5m - 1/2, 5n - 3/2)/\sqrt{5}$, $B = (5m + 3/2, 5n - 1/2)/\sqrt{5}$, $C = (5m - 3/2, 5n + 1/2)/\sqrt{5}$, and $D = (5m + 1/2, 5n + 3/2)/\sqrt{5}$, where, integers (m, n) labels the block position and the shortest Fe-Fe distance is set to be unit. Hence the model is invariant under translations $m \rightarrow m + 1$ or $n \rightarrow n + 1$ along either directions. We then let $t_{i,j} = t_1, t_2$ (or \tilde{t}_1, \tilde{t}_2) be the intra-block (or inter-block) nearest neighbor (n.n.) and the next nearest neighbor (n.n.n.) hopping amplitudes, illustrated in Fig.1(b). Notice that the n.n.n. hopping amplitudes are mainly due to the 3d-4p hybridization bridged by the Se-atoms above or below each blocks(not shown in Fig.1(a)), and in general, the vacancies will lead to structure distortions [8, 11, 16], breaking the degeneracy between the intra- and inter-block hopping amplitudes. While these hopping parameters can be determined by fitting the LDA band structures, our task here is to study the phase diagram for generic model parameters.

To begin with, we first exactly solve the non-interacting tight-binding model, $H_0 = \sum_{\vec{K}\lambda\sigma} c_{\lambda\sigma}^\dagger(\vec{K}) H_{\lambda\lambda'}(\vec{K}) c_{\lambda\sigma}(\vec{K})$, where, $c_{\lambda\sigma}(\vec{K})$ is the Fourier transformation of $c_{\lambda\sigma}(p)$ for an electron at the site λ in the p -th block, \vec{K} is in the first Brillouin zone (BZ) of the periodic blocks, $\lambda, \lambda' = A, B, C$ and D , and $H_{\lambda\lambda'} = [0, t_1 + \tilde{t}_2 e^{-iK_x}, t_1 + \tilde{t}_2 e^{-iK_y}, t_2 + \tilde{t}_1 e^{-iK_y}]; [t_1 + \tilde{t}_2 e^{iK_x}, 0, t_2 + \tilde{t}_1 e^{iK_x}, t_1 + \tilde{t}_2 e^{-iK_y}]; [t_1 + \tilde{t}_2 e^{iK_y}, t_2 + \tilde{t}_1 e^{-iK_x}, 0, t_1 + \tilde{t}_2 e^{-iK_x}]; [t_2 + \tilde{t}_1 e^{iK_y}, t_1 + \tilde{t}_2 e^{iK_x}, 0, t_1 + \tilde{t}_2 e^{iK_x}]]$. For simplicity, we assume $t_2/t_1 = \tilde{t}_2/\tilde{t}_1 = \alpha$, $\tilde{t}_1/t_1 = \tilde{t}_2/t_2 = \beta$ in the following discussions (setting $t_1 = 1$), the extensions to more generic cases are straightforward. Hence, α, β measure the strengths of hopping frustration (due to the Se-bridged hybridization) and the structure distortion (due to the Fe-vacancies) respectively. The obtained four bands $\varepsilon_{1,2,3,4}(\vec{K})$ are illustrated via the band structures and the density of state (DOS) for several sets of (α, β) , shown in Fig. 2(a-d). The sub-band gaps Δ_{12}, Δ_{34} as well as the mid-band gap Δ_{23} are plotted in Fig.3(a-c). We find that the system is always metallic at half-filling except for $\beta \lesssim 0.18$, where the mid-band gap Δ_{23} opens at the Fermi energy for $\alpha \gtrsim 1$.

On the other hand, in the large U limit, the n.n. and n.n.n. hoppings lead to the AFM exchanges ($J_1 = 4t_1^2/U$, $J_2 = 4t_2^2/U$) and ($\tilde{J}_1 = 4\tilde{t}_1^2/U$, $\tilde{J}_2 = 4\tilde{t}_2^2/U$) for the intra- and inter-block spins, respectively. The resulting spin Hamil-

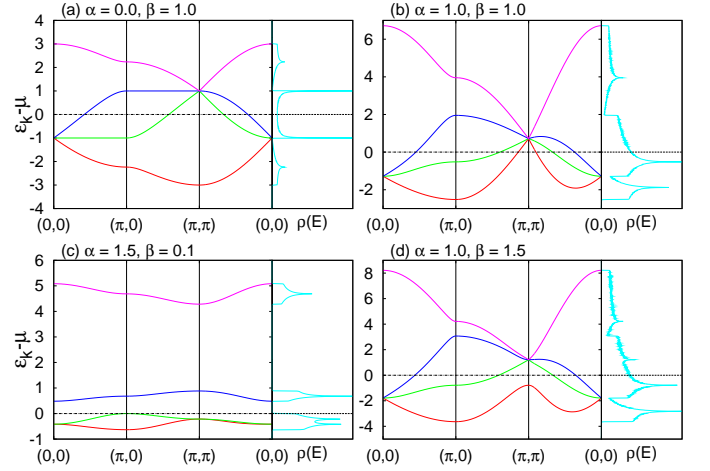


FIG. 2: (color online). Non-interacting band structures and DOS $\rho(E)$.

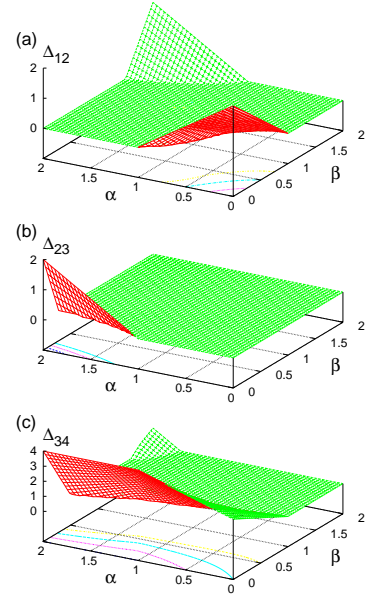


FIG. 3: (color online). Various non-interacting band gaps : (a) sub-band gap Δ_{12} ; (b) mid-band gap Δ_{23} ; (c) sub-band gap Δ_{34} .

tonian reads

$$H = \sum_p H_p + \sum_{p,q} H_{p,q}, \quad (2)$$

where

$$H_p = \left\{ \sum_{\lambda, \lambda' \in n.n.} J_1 + \sum_{\lambda, \lambda' \in n.n.n.} J_2 \right\} \vec{S}_\lambda(p) \cdot \vec{S}_{\lambda'}(p)$$

$$H_{p,q} = \left\{ \sum_{\lambda, \lambda' \in n.n.} \tilde{J}_1 + \sum_{\lambda, \lambda' \in n.n.n.} \tilde{J}_2 \right\} \vec{S}_\lambda(p) \cdot \vec{S}_{\lambda'}(q)$$

are the intra- and inter-block Hamiltonians, respectively, with $p, q = (m, n)$ being the n.n. blocks. The spin Hamiltonian is

well defined on the new bipartite lattice with AFM exchanges connecting the even and odd sublattices. It can be further shown that the lowest energy state has positive definite coefficients in the rotated Ising basis (obeying the Marshall's sign rule[17, 18]), hence the ground state is a singlet of the total spin $\sum_p \vec{S}_{block}(p)$, where $\vec{S}_{block}(p) = \sum_\lambda \vec{S}_\lambda(p)$ is the total spin in the p -th block. This implies that for each fixed λ -site, $\{\vec{S}_\lambda(p), \forall p\}$ forms a spin lattice of period $\sqrt{5} \times \sqrt{5}$, resulting in the Néel AFM orders in the classical limit [except for $\vec{S}_{block}(p) = 0$ where the ferromagnetic order is possible [18]], while the relative directions among different spins $\{\vec{S}_\lambda(p), \forall \lambda\}$ in a given block are dependent on the intra- and inter-block couplings. Notice that the block spin $\vec{S}_{block}(p)$ should not be understood as a single entity, since the interaction cannot be rewritten in terms of $\vec{S}_{block}(p)$. Rather, its formation is protected by the periodicity of the AFM bipartite lattice and a strong intra-block coupling is not a prerequisite. The expectation value of the block spin $\langle S_{block}^z(p) \rangle$ varies in between 0 and 2 and could reach the maximal magnitude when $2\vec{J}_2 + \vec{J}_1 \geq 2J_1 + J_2$.

We now consider the weak and intermediate U and solve the model by the MF method as applied to the conventional t_1 - t_2 Hubbard model[19–22]. We introduce the magnetic order parameters M_λ by writing

$$\langle 2S_\lambda^z(p) \rangle \equiv \langle n_{\lambda\uparrow}(p) \rangle - \langle n_{\lambda\downarrow}(p) \rangle = M_\lambda \cos(\vec{Q} \cdot \vec{r}(p)) \quad (3)$$

for each λ -sites, with $\vec{r}(p) = (m, n)$ being the position of the p -th block. We also consider the wavevector $\vec{Q} = (\pi, \pi)$, i.e., the Néel AFM ordering, for there is no direct coupling between the n.n.n. blocks. In our model, the collinear AFM ordering $\vec{Q} = (\pi, 0)$ (or $\vec{Q} = (0, \pi)$) may be favored when $\langle s_{block}^z(p) \rangle = 0$, and this case is simply identified with the collinear AFM in the t_2 - t_2 Hubbard (or J_1 - J_2 Heisenberg) model (without vacancies) favored for strong frustration t_2 (or J_2)[22, 23].

The MF approximation for the on-site repulsion U -term is standard, and diagonalization of the MF Hamiltonian is implemented over the first magnetic BZ zone of K -space (the reduced BZ for one of the sublattice). Eight bands of quasi-particles $E_{1,2,\dots,8}(\vec{K})$ are obtained, and the magnetic moments M_λ as functions of U are self-consistently determined by tuning the chemical potential μ at the half-filling. We first focus on the moderate frustration regime ($\alpha = 0.8$) with weak, moderate, and strong inter-block hopping amplitudes exemplified with (a) $\beta = 0.2$, (b) $\beta = 1$, and (c) $\beta = 1.5$, respectively. For each case, the magnetizations M_λ as well as the magnitude of the mid-band gap Δ at the Fermi energy as functions of U are shown in Fig. 4(a-c). We find that the four $M_{\lambda=A,B,C,D}$ are equal to each other in the calculated cases whereas they could be different in more generic cases. To draw the phase diagram, we perform the same calculations by varying the frustration $\alpha \sim 0-1.5$ for each fixed β . The AFM instability U_M and the MI transition point U_{MI} are determined by the onsets of magnetization and gap within the accuracy $\sim 10^{-6}$. For comparison, another point U_{vH} is marked at the

kink position in the magnetization curves in Fig.4. This point is identified as the van Hove singularity at the Fermi surface as evidenced by the corresponding band structures(not shown). Then, the $\alpha - U$ phase diagrams are plotted in Fig.5 for each cases. Notice that in Fig.5(c) the AFM metal region above the dashed line ($\alpha \lesssim 0.8$) may actually merge into the PM phase because the magnetization is vanishingly small within the calculation accuracy. Finally, three main aspects of these results are briefly discussed as follows.

(I) For moderate inter-block hopping ($\beta \sim 1$), the ground state is a PM metal for sufficiently small U and an AFM insulator for relatively large U . An extended intermediate AFM metallic phase emerges, separating the PM metal and AFM insulator phases in a wide range of frustration $\alpha \sim 0.5-1.5$. For instance, when $\alpha = 0.8$, we find $U_{MI} \sim 4.4$, and $U_M \sim 3.0$, respectively, while the van Hove singularity, which is located in between U_M and U_{MI} , could be clearly identified. It is worth noting that in the corresponding t_1 - t_2 Hubbard model without vacancies the Néel AFM metal phase is extremely narrow and is replaced by the collinear AFM metallic phase for $\alpha \gtrsim 0.7$ [22]. The corresponding $U_{MI} \sim 5.0$, $U_M \sim 3.6$. So we readily find that the Coulomb U needed for the Mott-transition is lowered from $U_{MI} \sim 5.0$ to $U_{MI} \sim 4.4$. A similar conclusion for U_{MI} is obtained by the spin-rotor MF theory for the two-orbital model appropriate for the iron-deficient ternary iron chalcogenides[9].

(II) In the strong inter-block hopping regime $\beta \sim 1.5$, the distinction between the PM and AFM metal phases is not significant, in particular for $\alpha \lesssim 0.8$, where the magnetization is vanishingly small. Thus in this regime, the AFM ordering immediately leads to the MI transition, and the van Hove singularity U_{vH} is also very close to U_{MI} . Another feature is that the U_{MI} shows a minimum in the moderate frustration regime around $\alpha \sim 0.8$, while the gap dependence on U is almost linear after the minimum. This feature resembles to that in the moderate inter-block hopping regime, see in Fig.4(b-c).

(III) When the non-interacting system is close to the band insulator phase, as in the case of weak inter-block hopping $\beta \sim 0.2$ and for $\alpha \lesssim 0.8$, we find that the band-gap opens at the Fermi energy immediately with very small U_{MI} , after the development of the Néel AFM order. The magnetization M_λ rapidly saturates to $1/2$, and the gap magnitude Δ , while being very small, keeps almost unchanged for further increase of U below a threshold value $U \sim 4.5$, manifesting itself as a conventional AFM semi-conductor. However, a drastic increase in M_λ is observed above this point, where it rapidly saturates further to the maximal value (defined as unit), see in Fig.4(a). Meanwhile, the gap increases almost linearly with the same tendency seen in (I) and (II). Moreover, the PM phase shrinks and U_{MI} increases for $\alpha \gtrsim 0.8$, so an intermediate AFM metal phase develops substantially in the strong frustration regime.

To summarize, we study the single-orbital Hubbard model on the square lattice with the tetragonal vacancy superstructure, the most perfect vacancy ordering pattern observed in the recently discovered iron deficient compounds

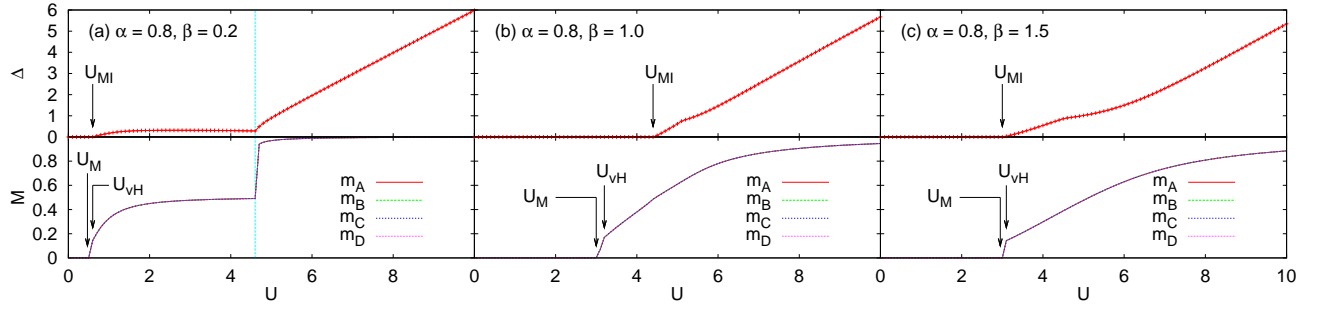


FIG. 4: (color online). U -dependences of magnetic moments M_λ and the mid-band gap Δ .

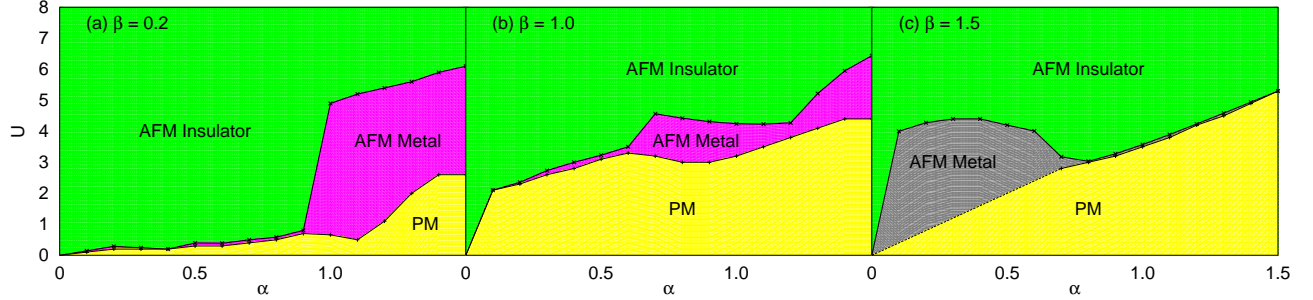


FIG. 5: (color online). Phase diagrams. The yellow, red, and green regions indicate the PM metal, AFM metal, and AFM insulator phases, respectively. Notice that in (c) the magnetization in the AFM metal region (pink region(light gray)) above the dashed line for $\alpha \lesssim 0.8$ is vanishingly small so that this AFM metal region may actually merge into the PM region (yellow region).

$(\text{A,Tl})_y\text{Fe}_{2-x}\text{Se}_2$. With increasing Coulomb interaction U the model shows a block-spin type Néel AFM order as a consequence of the vacancy symmetry. The MI transition takes place at a relatively small U_{MI} compared to the conventional Hubbard model without vacancies. But in a wide range of parameters an extended intermediate region of the metal phase with block-spin Néel AFM exists, separating the PM metal and AFM insulator phases. This feature is also in contrast to the models without vacancies. In some cases, an almost linear gap dependence on U accompanied by a broad crossover of the magnetization is observed slightly above U_{MI} and this behavior is indicative of the electron correlation effect within our MF approximation. An interesting exception is the case for the weak inter-block hopping regime, where drastic increases in both magnetization and gap magnitude are observed in the insulator phase. Previous LDA calculations suggest that inter-block n.n.n. AFM exchange \tilde{J}_2 dominates in the ground state of $(\text{A,Tl})_{0.8}\text{Fe}_{1.6}\text{Se}_2$ [11], indicating that the system should be in the strong inter-block hopping regime. While the multi-orbital characteristic and the Hund's rule coupling should be also taken into account for realistic materials, our results shed new light in understanding the electron correlation and the novel magnetism in the $(\text{A,Tl})_y\text{Fe}_{2-x}\text{Se}_2$ compounds.

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